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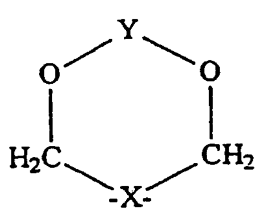


(I)

(57) Abstract: Catalyst composition based on (a) a Group VIII metal compound, (b) an anion, and (c) a ligand of the formula $R^1R^2M^1$-R^5-$M^2R^3R^4$, wherein R^1, R^2, R^3 and R^4 represent similar or different hydrocarbyl groups, which may optionally be substituted, M^1 and M^2 represent similar or different elements selected from arsenic, antimony, phosphorus and nitrogen and R^5 represents a bivalent bridging group in which the bridge consists of three atoms, the outer two of which are carbon atoms and the middle one (X) of which forms part of a group (I) wherein: X represents carbon or silicon; Y may represent a variety of groups and structures. The catalyst composition is particularly useful in the preparation of linear alternating polyketone polymers.

CATALYST COMPOSITION AND USE THEREOF

The present invention relates to catalyst compositions and their use as catalyst in the preparation of polyketone polymers.

Catalyst compositions for preparing polyketone polymers are known in the art. Typically, such catalyst compositions are based on a Group VIII metal compound, a bidentate ligand and an anion of an acid having a pKa of 6 or less. Bidentate ligands frequently used have the general formula $R_2M-R'-MR_2$, wherein each R independently represents an optionally substituted hydrocarbyl group, each M represents a chelating atom selected from arsenic, antimony, phosphorus and nitrogen and R' represents a bivalent bridging group, typically comprising from 1 to 4 atoms in the bridge, which atoms may or may not carry substituents. Carbon and silicon atoms often form the bridge, while the substituents, if any, normally consist of carbon and hydrogen and optionally oxygen.

Such a catalyst composition has many variables which could have an impact on the performance of the catalyst when preparing polyketones. Important variables in this respect are the Group VIII metal compound used, the type of anion used and in respect of the bidentate ligand: the groups attached to the chelating atoms and the bridging group. Important parameters defining the performance of the catalyst are bulk density of the polymer prepared and activity defined in terms of polymerization rate. In addition, other effects of using particular catalysts like fouling and building in of higher olefins into the polyketone polymer chain could be important. A general purpose of the present invention is to provide a catalyst

composition having an excellent performance in terms of both bulk density of the polymer formed and polymerization rate, but also in terms of reduced fouling, while the economics in relation to the catalyst composition should also be advantageous. Such economics, for instance, include the synthesis of the ligand and the costs associated therewith in terms of the number of synthesis steps required and the availability and prices of the various reactants.

In accordance with the present invention it was found that this overall purpose was best realised by using a specific ligand having a novel type of bridging group.

Bidentate ligands having specific bridging groups have been disclosed in various patent specifications, e.g. in EP-A-0,296,687.

In EP-A-0,296,687 catalyst compositions are disclosed wherein the bidentate ligand comprises a bivalent bridging group in which the bridge consists of three carbon atoms, the middle of which forms part of a group $-CR^7R^8-$ in which R^7 and R^8 are similar or different monovalent substituents exclusively comprising carbon, hydrogen and optionally oxygen. The most preferred bridging group clearly is the 2,2-dimethylpropylene group, which is used in all working examples of EP-A-0,296,687, as part of a phosphorus bidentate ligand containing phenyl or polar-substituted phenyl groups attached to the phosphorus atoms. As most suitable anions of acids para-toluene sulphonic acid anions and trifluoroacetic acid anions are mentioned. The catalyst compositions disclosed in EP-A-0,296,687 result in very good polymerization rates. No information, however, is given about the bulk density of the polymers formed.

The present invention aims to provide catalyst compositions which also have an excellent polymerization

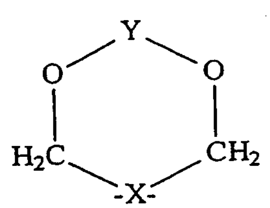
rate, but moreover also result in polyketone polymers having a high bulk density without significant fouling occurring. Furthermore, the present invention aims to provide a catalyst composition which is attractive from an economic perspective and can thus be obtained at relatively low cost.

Accordingly, the present invention relates to a catalyst composition based on

(a) a Group VIII metal compound,

(b) an anion, and

(c) a ligand of the formula $R^1R^2M^1-R^5-M^2R^3R^4$, wherein R^1, R^2, R^3 and R^4 represent similar or different hydrocarbyl groups, which may optionally be substituted, M^1 and M^2 represent similar or different elements selected from arsenic, antimony, phosphorus and nitrogen and R^5 represents a bivalent bridging group in which the bridge consists of three atoms, the outer two of which are carbon atoms and the middle one (X) of which forms part of a group



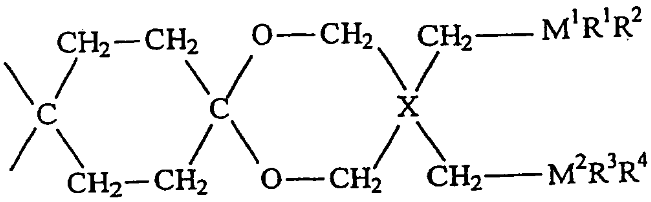
(I)

wherein:

X represents carbon or silicon;

Y represents

- a group $-C(R^6)(R^7)-$ or $-Si(R^6)(R^7)-$;
- a group $-P(R^8)-$ or $-P(O)(R^8)-$ or $-P(S)(R^8)-$;
- a group $-SO_2-$ or $-SO-$;
- a group $-Al(R^8)-$; or
- a group



(II)

with X, M^1, M^2, R^1, R^2, R^3 and R^4 as defined above;

R^6 and R^7:

- represent similar or different groups, oligomeric chains or polymeric chains exclusively comprising carbon, hydrogen and optionally one or more heteroatoms; or
- together with the carbon or silicon atom to which they are bonded form a cyclic aliphatic structure exclusively comprising carbon, hydrogen and optionally oxygen and/or silicon

with the proviso that R^6 and R^7 are not methyl groups if X is a carbon atom and the acid from which the anion is derived is para-toluenesulphonic acid or trifluoroacetic acid; and

R^8 represents hydrogen or an alkyl group having from 1 to 5 carbon atoms.

The Group VIII metal compound used as component (a) may be a platinum, cobalt, nickel or palladium compound, preferably a palladium compound. This compound may take the form of a salt of a carboxylic acid, with an acetate being preferred. The most preferred Group VIII metal compound is palladium acetate.

The skilled person will appreciate that in favour of a high polymerisation rate the anion used as component (b) should not or only weakly co-ordinate with the Group VIII metal. Examples of suitable anions are anions of protic acids, including acids which are obtainable by combining a Lewis acid and a protic acid, and acids which are adducts of boric acid and a 1,2-diol, a catechol or a

salicylic acid. Preferred acids are those acids which have a pKa of less than 6, in particular less than 4, more in particular less than 2, when measured in an aqueous solution at 18 °C. Examples of suitable acids are known in the art and include sulphuric acid, perchloric acid, sulphonic acids, such as methane sulphonic acid and para-toluenesulphonic acid, and carboxylic acids, such as 2,6-dihydroxybenzoic acid, maleic acid, trichloroacetic acid, difluoroacetic acid and trifluoroacetic acid. An example of an acid which is a combination of a Lewis acid (BF_3) with a protic acid (HF) is tetrafluoroboric acid (HBF_4). Other suitable anions are borate anions comprising the same or different hydrocarbyl groups attached to boron, such as tetraarylborates and carborates. Hydrocarbylboranes, such as e.g. triphenylborane, or aluminoxanes, such as methyl aluminoxanes and tert.-butyl aluminoxanes, may also be applied as compounds functioning as a source of anions. More examples of suitable anions are given in EP-A-0,743,336. For the purpose of the present invention the anion most preferably originates from a protic acid selected from para-toluenesulphonic acid, trifluoroacetic acid, maleic acid and mixtures of two or more of these.

In this connection it was also found that particularly maleic acid had a beneficial effect on various properties, such as the oxidative stability and whiteness of the polyketone polymers prepared. This beneficial effect was found not to be limited to the specific ligands which are the subject of the present application, but to extend beyond these ligands to other ligands as well. Hence, said beneficial effects were concluded to be attributable to the use of maleic acid as the anion source.

The quantity of the source of anions is suitably selected such that it provides in the range of from 0.1 to 50, preferably from 0.5 to 25, equivalents of anions per mole of Group VIII metal. However, aluminoxanes may be used in such a quantity that the molar ratio of aluminium to the Group VIII metal is in the range of from 4000:1 to 10:1, preferably from 2000:1 to 100:1, most preferably from 500:1 to 200:1.

In the ligand forming component (c) of the present catalyst composition the groups R^1, R^2, R^3 and R^4 preferably represent similar or different aryl groups, which may optionally be substituted with one or more substantially apolar and/or one or more polar groups. In an even more preferred embodiment R^1, R^2, R^3 and R^4 independently represent a phenyl group or a substituted phenyl group, wherein in the latter case one or more substituents selected from C1-C4 alkoxy groups, most suitably a methoxy group, aryloxy groups, most suitably a phenyloxy group, and C1-C4 alkyl groups, most suitably a methyl group, are present. Examples of suitable substituted groups are 2-methoxyphenyl, 2,4-dimethoxyphenyl, 4-methoxyphenyl, 2,6-dimethoxyphenyl, 2-methoxy-5-methylphenyl and 2,4,6-trimethoxyphenyl. Most preferably all groups R^1, R^2, R^3 and R^4 are identical and are selected from phenyl, 2-methoxyphenyl and 2-methoxy-5-methylphenyl.

The central atom X of the ligand's bridge can be either a carbon atom or a silicon atom, but preferably it is a carbon atom. Chelating atoms M^1 and M^2 preferably both are phosphorus atoms.

The central atom X of the bridging group forms part of a cyclic structure as indicated in formula (I). This cyclic structure is completed by the group Y. The group Y present in the ligand may represent a variety of

different groups, which are able to form two stable bonds with both oxygen atoms indicated in formula (I), so that a stable cyclic structure can be formed. Accordingly, the group Y may represent the groups indicated above. First of all, Y may represent a group $-C(R^6)(R^7)-$ or $-Si(R^6)(R^7)-$ wherein R^6 and R^7 either represent similar or different groups or chains exclusively comprising carbon, hydrogen and optionally one or more heteroatoms, or together with the carbon atom to which they are bonded form a cyclic aliphatic structure exclusively comprising carbon, hydrogen and optionally oxygen with the proviso that R^6 and R^7 are not methyl groups if X is a carbon atom and the acid from which the anion (component (b)) is derived is para-toluenesulphonic acid or trifluoroacetic acid.

In one preferred embodiment R^6 and R^7 independently represent alkyl groups or polymeric chains comprising carbon, hydrogen and optionally one or more heteroatoms, such as oxygen, nitrogen, sulphur and phosphorus. Of these, C1-C4 alkyl groups, such as methyl or ethyl, or polyketone polymeric chains, i.e. polymeric chains comprising one or more carbonyl groups either in an alternating fashion with the olefinic comonomer(s) or in a random distribution across the polymer chain. The length of these polymeric chains may vary within broad limits and includes both oligomers and polymers. If R^6 and R^7 are polyketone polymeric chains, these chains may serve as a carrier to which the ligand is covalently bonded. In this way a catalyst supported on a carrier can be obtained. Such catalysts are specifically of interest for gas phase polymerization processes, although they may also be useful in liquid phase (or slurry) polymerization processes for preparing linear alternating polyketone polymers.

Furthermore, if R^6 and R^7 are polyketone polymeric chains more than one ligand may be bonded to a single polymer chain. Accordingly, in a suitable embodiment of the present invention one polymeric chain may serve as a "backbone" from which two or more ligands of formula (I) are pending. In fact, these ligands are bonded to the polyketone backbone polymer via the keto group: Y in formula (I) is the carbon atom of the original keto group in the polymer chain.

In another preferred embodiment R^6 and R^7 together with the carbon atom to which they are bonded form a cycloalkyl group, which may optionally be substituted with one or more substantially apolar or polar groups. Substantially apolar substituents include alkyl groups, preferably C1-C4 alkyl groups, of which methyl and ethyl are most preferred. Suitable polar substituents include inter alia alkoxy groups (suitably C1-C4 alkoxy groups like methoxy and ethoxy), oxo groups, hydroxy groups and carboxyl groups. Preferably, however, R^6 and R^7 together with the carbon atom to which they are bonded form a cycloalkyl group, most preferably a cyclopentyl or cyclohexyl group.

In general, ligands with X being a carbon atom and Y representing $-C(R^6)(R^7)-$ as discussed above can be prepared by a process comprising the steps of:

(a) reacting the commercially available 2,2-bis(bromomethyl)-1,3-propanediol with a compound $R^6-C(=O)-R^7$; and subsequently

(b) reacting the compound thus obtained with the chelating atom-containing compounds, such as $Li-M^1R^1R^2$ and/or $Li-M^2R^3R^4$ and recovering the ligand.

This process is further referred to as Method I.

Step (a) can be carried out by methods known in the art. For instance, in Example 1 of US-4,851,461 this

reaction is exemplified for cyclohexanone. Process conditions typically include a temperature of 10 to 160 °C and a pressure of from essentially zero to 10 bar. Preferably, step (a) is carried out at an elevated temperature of at least 60 °C at atmospheric pressure. Step (b) can, for instance, be effectively carried out in accordance with the process disclosed in European patent application No. 98203587 disclosing both the preparation of compounds of the type Li-$M^1R^1R^2$ and the reaction of halogen-containing compounds with these lithium compounds, thereby producing dentate ligands useful as catalyst component in catalyst compositions for producing polyketone polymers. Suitably, step (b) is carried out at a temperature not exceeding 55 °C, preferably not exceeding 40 °C, and especially not exceeding 30 °C. Suitably the process is carried out at a temperature of at least -50 °C, preferably at least -15 °C and most preferably at least 0 °C. Cooling is generally required for such a process, whereby the temperature of the reaction mixture is preferably between 0 and 25 °C. The pressure is not particularly critical and may vary from essentially zero to 10 bar. Suitably, this process step is carried out at a pressure of from 0.5 to 1.5 bar.

Alternatively, ligands with X being a carbon atom and Y representing -C(R^6)(R^7)- as discussed above can be prepared by a process (Method II) comprising the steps of:

(a) reacting the commercially available 2,2-bis(bromomethyl)-1,3-propanediol with a protective agent which will react with the hydroxyl groups;

(b) reacting the product of step (a) with the chelating atom-containing compounds, such as Li-$M^1R^1R^2$ and/or Li-$M^2R^3R^4$;

(c) removing the protective agent from the hydroxyl groups; and

(d) reacting the product of step (c) with a compound R^6-C(=O)-R^7 and recovering the ligand.

Protecting the hydroxyl groups of a 1,3-diol by a chemical reaction is well known in the art. Suitable protective agents include, for instance, ketones (thus forming a ketal) and aldehydes (thus forming an acetal). Examples of suitable protective agents are propanone, formaldehyde and ethanal. Removal of the protective agents after step (b) can e.g. suitably be effected by adding acid. Such methods are also well known in the art. Steps (b) and (d) can be carried out under the same conditions as outlined herein before.

Similarly, ligands with Y representing -Si(R^6)(R^7)- as discussed above can be prepared by Method I or Method II, wherein (R^6)(R^7)$SiCl_2$ is used instead of R^6-C(=O)-R^7. An example of a commercially available compound (R^6)(R^7)$SiCl_2$ is diethylsilicondichloride.

Furthermore, Y may also represent one of the following groups:

(i) a group -P(R^8)- or -P(O)(R^8)- or -P(S)(R^8)-;

(ii) a group -SO_2- or -SO-; or

(iii) -Al(R^8)-

wherein R^8 represents hydrogen or an alkyl group having from 1 to 5 carbon atoms. Ligands with any one of these groups Y can also be prepared in a relatively simple and cost-effective manner by Method I or Method II. More particularly, a ligand of formula I with Y representing -P(R^8)- can be effectively prepared by Method I or Method II employing a dihalophosphine (e.g. R^8-PCl_2) instead of R^6-C(=O)-R^7. Ligands of formula I with Y representing

$-P(O)(R^8)-$; or $-P(S)(R^8)-$; $-SO_2-$; $-SO-$ or $-Al(R^8)-$ are most suitably prepared by Method II using respectively a dihalophosphinoxide (e.g. R^8-POCl_2 or R^8-POBr_2) a dihalophosphine sulphide (e.g. R^8-PSCl_2 or R^8-PSBr_2), sulphuryl chloride (SO_2Cl_2), thionyl chloride ($SOCl_2$) or ethylaluminium dichloride ($C_2H_5AlCl_2$) instead of $R^6-C(=O)-R^7$.

In a further embodiment Y may represent the group indicated by formula (II). In this case a tetradentate ligand is obtained. A compound of formula (II) may suitably be obtained via Method I by reacting two moles of 1,3-dibromo-2,2-dihydroxymethylene-propane with one mole of 1,4-cyclohexanedione followed by the reaction with the chelating atom-containing compounds.

The ligands are suitably used in the catalyst composition in a quantity of from 0.5 to 2 and in particular of from 0.75 to 1.5 mole per mole of Group VIII metal.

Organic oxidant promoters may be incorporated into the catalyst composition in order to enhance their performance. Examples of suitable promoters are quinones, such as benzoquinone, naphthoquinone and anthraquinone. The amount of promoter used is suitably in the range of from 1 to 250, preferably 1 to 100, mole per mole of Group VIII metal.

The catalyst composition of the present invention is suitably used in the form of a solution in a liquid. Suitable liquids include polar liquids, such as C_1-C_4 alcohols, for example methanol and ethanol, C_2-C_8 ethers such as diethylether, tetrahydrofuran or the dimethylether of diethylene glycol (diglyme), C_2-C_6 ketones such as acetone and methylethylketone and aromatic solvents such as toluene. For the purpose of the present invention

methanol and acetone are preferred. The present invention also relates to a solution of the catalyst composition described above.

In a further aspect the present invention also relates to novel compounds of the formula $R^1R^2M^1-R^5-M^2R^3R^4$, wherein R^1, R^2, R^3, R^4, M^1, M^2 and R^5 have the same meaning as indicated above with the proviso that R^6 and R^7 are not methyl groups if X is a carbon atom. In a much preferred embodiment R^6 and R^7 represent similar or different C_1-C_4 alkyl groups, preferably methyl or ethyl, or polyketone polymer chains or together with the carbon atom to which they are bonded form a cyclopentyl or cyclohexyl group.

The invention also relates to a process for the preparation of polymers, wherein a mixture of carbon monoxide and one or more olefinically unsaturated compounds is polymerised in the presence of a catalyst composition as defined above.

Olefinically unsaturated compounds which can be used as monomers in the said process include compounds consisting exclusively of carbon and hydrogen and compounds which in addition comprise heteroatoms, such as unsaturated esters, ethers and amides. Unsaturated hydrocarbons are preferred. Examples of suitable olefinic monomers are olefins, such as ethene, propene, butene-1, octene-1, decene-1 and dodecene-1, cyclic olefins such as cyclopentene, aromatic compounds, such as styrene and α-methylstyrene and vinyl esters, such as vinyl acetate and vinyl propionate. Most preference is given to ethene and mixtures of ethene with another olefinically unsaturated compound, in particular an α-olefin, such as propene, butene-1, octene-1, decene-1 and dodecene-1.

Generally, the molar ratio of on the one hand carbon monoxide and on the other hand the olefinically

unsaturated compound(s) used as monomer is selected in the range of 1:5 to 5:1. Preferably the molar ration is in the range of 1:2 to 2:1, substantially equimolar rations being preferred most.

The process according to the invention is suitably carried out at an overall pressure of from 20 to 150 bar. However, for economic reasons overall pressures between 20 and 75 bar are usually preferred. The polymerization is usually carried out at a temperature in the range of from 20 to 200 °C, preferably 40 to 150 °C.

The present process may be carried out as a gas phase polymerization, as a super critical phase polymerization and as a liquid phase or slurry polymerization. When carried out as a gas phase process, the catalyst composition is suitably supported on a carrier. Suitable carrier materials and methods and means for impregnating a carrier with catalyst solution are well known in the art. When carried out in the supercritical phase, suitable diluents would be ethene or carbon dioxide. When carried out as a slurry process, the diluent used should be a liquid in which the polyketone polymers formed are essentially insoluble such that they form a suspension. Suitable diluents are ketones (e.g. acetone), chlorinated hydrocarbons (e.g. chloroform or dichloromethane), aromatics (e.g. toluene, benzene, chlorobenzene) and protic diluents, such as C1-C4 alcohols (e.g. methanol and ethanol). Mixtures of liquid diluents may be used as well, for example protic diluents may comprise an aprotic diluent. Of these diluents the C1-C4 alcohols, and in particular methanol, are preferred.

The quantity of catalyst composition used in the process of the present invention suitably is such that per mole of olefinically unsaturated compound to be copolymerized 10^{-7} to 10^{-3} and particularly 10^{-6} to 10^{-4}

mole of Group VIII metal is present. The polymerization process according to the present invention may be carried out either batchwise or continuously.

The invention will now be illustrated with the following examples without limiting the invention to these specific embodiments. In these examples the Limited Viscosity Number (LVN) of polymers is reported. The concept of LVN is well known in the art and is extensively explained in e.g. EP-A-0,246,674 and EP-A-0,319,083. The LVN referred to in the present application corresponds with the LVN as explained in EP-A-0,319,083, i.e. an LVN on the basis of the viscosities determined at 60 °C of four solutions of the polymer prepared by dissolving the polymer in four different concentrations at 60 °C in m-cresol.

Example 1 (for comparison)

2,2-dimethyl-1,3-bis(bis(o-anisyl)phospino)propane was prepared via the following intermediates in the ways indicated:

a) 2,2-dimethyl-1,3-propanediol dimesylate

A 1 litre reaction vessel equipped with a mechanical stirrer and a dropping funnel was charged with 33.3 g (0.32 mole) of 2,2-dimethyl-1,3-propanediol, 72.7 g (0.72 mole) of triethylamine and 250 ml of dichloromethane. The mixture was cooled to 0 °C and 82.4 g (0.72 mole) of methanesulfonyl chloride was added at such a rate that the temperature remained between 0 and 10 °C. The resulting mixture was stirred for one more hour at room temperature. Subsequently, 200 ml of water were added. The organic layer was separated and washed with two additional 200 ml portions of water. The organic layer was dried over anhydrous $MgSO_4$, filtered over a P3 glass frit and evaporated to dryness. Finally, the residue was slurried with 500 ml of hexane, yielding

74.1 g (0.285 mol, 89%) of 2,2-dimethyl-1,3-propanediol dimesylate.

b) 1,3 dibromo-2,2-dimethylpropane

A 1 litre reaction vessel equipped with a mechanical stirrer was charged with 74.1 g (0.285 mole) of 2,2-imethyl-1,3-propanediol dimesylate, 50 g (0.57 mole) of anhydrous lithium bromide and 500 ml of N,N-iethyl-acetamide. The mixture was stirred for 6 hours at 120 °C. After cooling, the reaction mixture was transferred to a separating funnel and 1 litre of water and 500 ml of hexane were added. The hexane layer was separated off and washed with two additional 500 ml portions of water. The hexane layer was subsequently dried over anhydrous $MgSO_4$, filtered over a P3 glass frit and evaporated to dryness. The residue was distilled under vacuum, yielding 56.1 g (0.244 mol, 86 %) of 1,3-ibromo-2,2-dimethylpropane.

c) 2,2-dimethyl-1,3-bis(bis(o-anisyl)phospino)propane

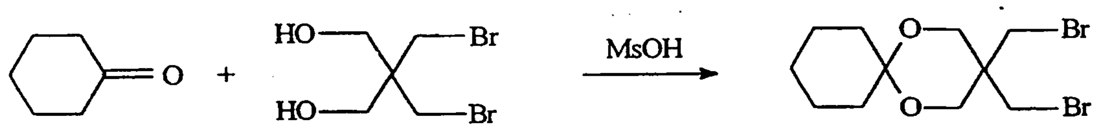
A 100 ml reaction vessel under argon atmosphere and equipped with a mechanical stirrer and a reflux condensor is charged with 40 ml of THF, 3.17 g (10 mmole) of N,N-diethylamino-bis(2-anisyl)phosphine and 486 mg (21 mmole) of a 30 % lithium dispersion under argon atmosphere at 0 °C. The reaction mixture was stirred for 16 hours after which time a precipitate had been formed. ^{31}P NMR indicated full conversion of the starting phosphine. Next, 5 ml of DMSO were added, followed by slow addition of 1.15 g (5 mmole) of 1,3-dibromo-2,2-dimethylpropane. After stirring for two more hours 20 ml of methanol was added and the solvents were removed under vacuum. To the residue 50 ml of dichloromethane and 50 ml of water were added. The dichloromethane phase was separated off and washed with 25 ml of water. The organic phase was subsequently dried over anhydrous $MgSO_4$, filtered over a P3 glass frit and evaporated to dryness

under vacuum at 20 °C. The residue was refluxed in 10 ml of methanol yielding a white precipitate. After filtration and drying the desired diphospine was obtained in a yield of 1.73 g (3.1 mmole, corresponding to 62% yield) as a white solid, which was pure according to ^{1}H, ^{13}C and ^{31}P NMR.

Example 2

3,3-bis-[bis-(2-methoxyphenyl)-phosphanylmethyl]-1,5-dioxa-spiro[5.5]undecane was prepared via the following intermediates in the ways indicated:

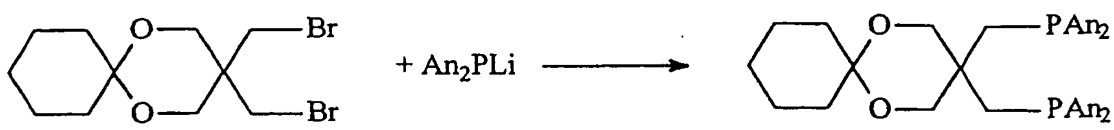
a) 3,3-bis-bromomethyl-1,5-dioxa-spiro[5.5]undecane was prepared via the following reaction ("MsOH" stands for methanesulfonic acid):



A mixture of 52.4 gr. (0.2 mole) of 2,2-bis(bromo-methyl)-1,3-propanediol, 19.6 gr. (0.2 mole) of cyclo-hexanone, 200 ml toluene and 0.5 ml of methanesulfonic acid was refluxed for two hours using a Dean Stark apparatus, during which time the theoretical amount of water (3.6 ml; 0.2 mole) was collected. After cooling the mixture was extracted with 200 ml of a dilute sodium bicarbonate solution and 2 x 100 ml water. The organic layer was dried on anhydrous $MgSO_4$, filtrated over a G3 glass filter and concentrated. The yield is virtually quantitative.

Analysis with gas chromatography indicated a purity of 98% (in toluene as solvent).

b) 3,3-bis-[bis-(2-methoxyphenyl)-phosphanylmethyl]-1,5-dioxa-spiro[5.5]undecane was obtained through the following reaction ("An" stands for anisyl, which is a 2-methoxyphenyl group):



A 100 ml reaction vessel equipped with a mechanical stirrer and a reflux condensor was charged with 40 ml of THF, 3.17 g (10 mmole) of N,N-diethylamino-bis(2-anisyl)-phosphine and 486 mg (21 mmole) of a 30% lithium dispersion under argon atmosphere at 0 °C. The reaction mixture was stirred for 16 hours after which time a thick precipitate had formed. ^{31}P NMR indicated full conversion of the starting phosphine.

Lithium diethylamide was quenched by addition of 535 mg (10 mmole) of ammoniumchloride, which caused a temperature rise to 6 °C. The mixture was cooled again to 0 °C, stirred for 30 more minutes and 1.71 g (5 mmole) of the compound (a) in 5 ml of THF was added over a period of 10 minutes. The mixture was stirred for two more hours while the temperature was slowly raised to 20 °C. Next 10 ml of methanol were added, the solvent was removed under vacuum and 40 ml of toluene and 40 ml of water were added. The organic phase was separated off and washed with 20 ml of water. The toluene phase was concentrated to 10 ml, 30 ml of methanol were added and the mixture was refluxed until a white precipitate appeared. The mixture was allowed to crystallize overnight. Hereafter it was filtrated over a P3 glass frit, rinsed with methanol and dried.

The desired diphosphine was obtained in a yield of 2.54 g (76 % yield) as a white solid, which was pure according to ^{1}H, ^{13}C and ^{31}P NMR.

Example 3 Preparation of Catalyst Solution I

Palladium acetate (16.9 mg, 0.0752 mmole) was added to 20 ml of acetone. After 5 minutes all solids were

dissolved to give an orange solution. Subsequently, 53.1 mg (0.0789 mmole) of the ligand prepared in Example†2 was added. Within a few minutes a clear yellow solution was obtained. After 1 hour, trifluoroacetic acid (51.4 mg, 34.8 ml, 0.451 mmole) was added. The solution was stirred for 1 hour and a clear, slightly yellow solution was obtained.

When kept at room temperature, it was found that this solution was stable for at least 4 weeks.

Example 4 Preparation of Catalyst Solution II

Example 3 was repeated except that maleic acid was added instead of trifluoroacetic acid. Accordingly, a catalyst solution was prepared on the basis of:
16.9 mg (0.0752 mmole) palladium acetate,
53.1 mg (0.0789 mmole)of the ligand of Example 2,
175 mg (1.50 mmole) maleic acid and
20 ml acetone.

When kept at room temperature, it was found that this solution was also stable for at least 4 weeks.

Example 5 Polymerization

Seed powder (5.4 g, ethene/propene/CO terpolymer, 2 wt% propene) was weighed directly into in a 0.5 l autoclave followed by 270 g (334 ml) of methanol. Catalyst Solution I was introduced via a polyethene syringe. The autoclave was closed, the stirrer was turned on and the system was pressurized to 50 bar nitrogen to leak-test the reactor and to remove the greater part of oxygen. After 5 minutes the pressure was carefully released. The heating mantle was switched on, and when the temperature reached 88 °C 24 bar ethene was added, followed by 24 bar carbon monoxide, so that the total pressure was 50 bara (autogeneous pressure of methanol is 2 bar). During the run a 1:1 (mole/mole) gas mixture of CO/ethene was introduced to keep the pressure at 50 bar

throughout the polymerization. The polymerization was considered to start (t=0) when the CO was introduced.

The polymerization proceeded at 90° C for 1 hour. Then, the heating was stopped, the reactor cooling was switched on and the pressure was carefully released. The polymer was filtered off using a Büchner funnel, washed with methanol and dried overnight in the vacuum oven.

The mass of CO/ethene (CO/E) copolymer obtained was determined and corrected for the seed powder, and the bulk density and LVN were measured. The results are indicated in Table I.

Example 6

Example 5 was repeated except that Catalyst Solution II was used instead of Catalyst Solution I. The results are indicated in table I.

Example 7 (for comparison)

Example 5 was repeated except that instead of Catalyst Solution I a catalyst solution was added based on:

0.0752 mmole palladium acetate,
0.0789 mmole of the ligand prepared in Example 1,
0.451 mmole trifluoroacetic acid, and
20 ml acetone.

The mass of polymer obtained was determined and corrected for the seed powder, and the bulk density and LVN (at 60 °C in m-cresol) were measured. The results are indicated in Table I.

Example 8 Polymerization

Seed powder (33.6 g ethene/propene/CO terpolymer, 6 wt% propene) was weighed directly into a 1.25 l autoclave the autoclave followed by 560 g (693 ml) methanol and 11.2 g water. Catalyst Solution I was introduced via a polyethene syringe. The autoclave was closed, the stirrer was turned on and the system was pressurized to 50 bar nitrogen to leak-test the reactor

and to remove most of the oxygen present. After 5 minutes the pressure was carefully released and the reactor was flushed three times with CO. Subsequently, 72 g of liquid propene were added followed by 10 bars of CO. The heating mantle was switched on, and when the temperature reached 76 °C ethene was added to arrive at a final pressure of 46 bar. This resulted in a CO/olefin molar ratio of 0.7 and an ethene/propene molar ratio of 0.4 (autogenous pressure of methanol is 2 bar). During the polymerization a 1:1 (mole/mole) gas mixture of CO/ethene was introduced to keep the pressure at 46 bar throughout the polymerization. The polymerization was considered to have begun when the CO was introduced.

The polymerization proceeded at 76 °C for 6 hours. Then, the heating was stopped, the reactor cooling was switched on and the pressure was carefully released. The polymer was filtered off using a Büchner funnel, washed with methanol and dried overnight in a vacuum oven. The mass of CO/ethene/propene (CO/E/P) terpolymer obtained was recorded and corrected for the seed powder, and the bulk density and LVN (at 60 °C in m-cresol) were measured. the results are indicated in Table I.

Example 9

Example 8 was repeated except that Catalyst Solution II was used instead of Catalyst Solution I. The results are indicated in Table I.

Example 10 (for comparison)

Example 6 was repeated except that instead of Catalyst Solution I a catalyst solution was added based on:

0.0752 mmole palladium acetate,
0.0789 mmole of the ligand prepared in Example 1,
0.451 mmole trifluoroacetic acid, and
20 ml acetone.

The mass of polymer obtained was determined and corrected for the seed powder, and the bulk density and LVN were measured. The melting point (m.p.) was also determined. The results are indicated in Table I.

Table I Polymerization results

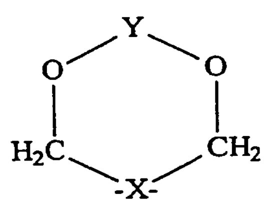
Example	Polymer	Rate (kg/g.h)	LVN (dl/g)	m.p. (°C)
5	CO/E	44	1.20	n.d.
6	CO/E	33	1.27	n.d.
7*	CO/E	25	1.35	n.d.
8	CO/E/P	11.5	1.33	221
9	CO/E/P	10.9	1.20	225
10*	CO/E/P	10.5	1.44	228

* for comparison

The results in Table I show that the catalyst composition according to the present invention produces polyketone polymers of sufficiently high molecular weight (as expressed in terms of LVN) at a high rate.

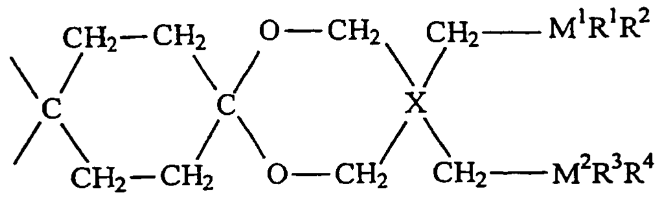
CLAIMS

1. Catalyst composition based on
(a) a Group VIII metal compound,
(b) an anion, and
(c) a ligand of the formula $R^1R^2M^1\text{-}R^5\text{-}M^2R^3R^4$, wherein R^1, R^2, R^3 and R^4 represent similar or different hydrocarbyl groups, which may optionally be substituted, M^1 and M^2 represent similar or different elements selected from arsenic, antimony, phosphorus and nitrogen and R^5 represents a bivalent bridging group in which the bridge consists of three atoms, the outer two of which are carbon atoms and the middle one (X) of which forms part of a group



(I)

wherein:
X represents carbon or silicon;
Y represents
- a group $-C(R^6)(R^7)-$ or $-Si(R^6)(R^7)-$;
- a group $-P(R^8)-$ or $-P(O)(R^8)-$ or $-P(S)(R^8)-$;
- a group $-SO_2-$ or $-SO-$;
- a group $-Al(R^8)-$; or
- a group



(II)

with X, M^1, M^2, R^1, R^2, R^3 and R^4 as defined above;

R^6 and R^7:

- represent similar or different groups, oligomeric chains or polymeric chains exclusively comprising carbon, hydrogen and optionally one or more heteroatoms; or
- together with the carbon or silicon atom to which they are bonded form a cyclic aliphatic structure exclusively comprising carbon, hydrogen and optionally oxygen and/or silicon

with the proviso that R^6 and R^7 are not methyl groups if X is a carbon atom and the acid from which the anion is derived is para-toluenesulphonic acid or trifluoroacetic acid; and

R^8 represents hydrogen or an alkyl group having from 1 to 5 carbon atoms.

2. Catalyst composition as claimed in claim 1, wherein the Group VIII metal compound is a palladium compound.

3. Catalyst composition as claimed in claim 1 or 2, wherein component (b) is an anion of an acid having a pKa of less than 6, preferably of less than 4.

4. Catalyst composition as claimed in claim 3, wherein the acid is selected from para-toluenesulphonic acid, trifluoroacetic acid, maleic acid and mixtures of two or more of these.

5. Catalyst composition as claimed in any one of claims 1-4, wherein in the bidentate ligand the groups R^1, R^2, R^3 and R^4 represent similar or different aryl groups,

which may optionally be substituted with one or more substantially apolar and/or one or more polar groups.

6. Catalyst composition as claimed in claim 5, wherein the groups R^1, R^2, R^3 and R^4 represent phenyl groups, which may optionally be substituted with one or more substituents selected from C1-C4 alkyl groups, preferably methyl, aryloxy groups, preferably phenyloxy, and C1-C4 alkoxy groups, preferably methoxy.

7. Catalyst composition as claimed in claim 6, wherein the groups R^1, R^2, R^3 and R^4 are identical and are selected from phenyl, 2-methoxyphenyl and 2-methoxy-5-methylphenyl groups.

8. Catalyst composition as claimed in any one of the preceding claims, wherein X represents a carbon atom.

9. Catalyst composition as claimed in any one of claims 1-8, wherein Y represents a group $-C(R^6)(R^7)-$.

10. Catalyst composition as claimed in claim 9, wherein R^6 and R^7 independently represent alkyl groups or polymeric chains comprising carbon, hydrogen and optionally oxygen.

11. Catalyst composition as claimed in claim 10, wherein R^6 and R^7 independently represent methyl or ethyl or polyketone polymer chains.

12. Catalyst composition as claimed in claim 9, wherein R^6 and R^7 together with the carbon atom to which they are bonded form a cycloalkyl group, which may optionally be substituted with one or more substantially apolar or polar groups.

13. Catalyst composition as claimed in claim 12, wherein R^6 and R^7 together with the carbon atom to which they are bonded form a cyclopentyl or cyclohexyl group.

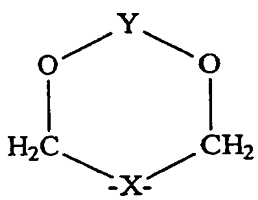
14. Catalyst solution comprising a catalyst composition as claimed in any one of claims 1-13 dissolved in a suitable liquid.

15. Catalyst solution as claimed in claim 14, wherein the liquid is methanol or acetone.

16. Compounds of the formula $R^1R^2M^1-R^5-M^2R^3R^4$, wherein R^1, R^2, R^3, R^4, M^1, M^2 and R^5 are as defined in claim 1.

17. Compound as claimed in claim 16, wherein Y represents a group $-C(R^6)(R^7)-$ and R^6 and R^7 represent similar or different C1-C4 alkyl groups, preferably methyl or ethyl, or polyketone polymer chains or together with the carbon atom to which they are bonded form a cyclopentyl or cyclohexyl group.

18. Process for the preparation of compounds of the general formula $R^1R^2M^1-R^5-M^2R^3R^4$, wherein R^1, R^2, R^3, R^4, M^1, and M^2 are as defined in claim 1 and R^5 represents a bivalent bridging group in which the bridge consists of three atoms, the outer two of which are carbon atoms and the middle one (X) of which forms part of a group



(I)

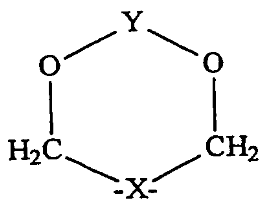
with X being a carbon atom and Y representing $-C(R^6)(R^7)-$, $-Si(R^6)(R^7)-$ or $-P(R^8)-$ wherein R^6, R^7 and R^8 have a meaning as defined in claim 1, which process comprises the steps of:

(a) reacting 2,2-bis(bromomethyl)-1,3-propanediol with a compound $R^6-C(=O)-R^7$; $(R^6)(R^7)SiCl_2$ or a dihalophosphine and subsequently

(b) reacting the compound thus obtained with the chelating atom-containing compounds, preferably $Li-M^1R^1R^2$ and/or $Li-M^2R^3R^4$, and recovering the ligand.

19. Process for the preparation of compounds of the general formula $R^1R^2M^1-R^5-M^2R^3R^4$, wherein R^1, R^2, R^3, R^4,

M^1, and M^2 are as defined in claim 1 and R^5 represents a bivalent bridging group in which the bridge consists of three atoms, the outer two of which are carbon atoms and the middle one (X) of which forms part of a group



(I)

with X being a carbon atom and Y representing one of the following groups:

(i) $-P(O)(R^8)-$ or $-P(S)(R^8)-$;

(ii) $-SO_2-$ or $-SO-$; or

(iii) $-Al(R^8)-$

wherein R^8 has a meaning as defined in claim 1, which process comprises the steps of:

(a) reacting 2,2-bis(bromomethyl)-1,3-propanediol with a protective agent which will react with the hydroxyl groups;

(b) reacting the product of step (a) with the chelating atom-containing compounds, preferably $Li\text{-}M^1R^1R^2$ and/or $Li\text{-}M^2R^3R^4$;

(c) removing the protective agent from the hydroxyl groups; and

(d) reacting the product of step (c) with a dihalophosphinoxide ($R^8\text{-}POCl_2$ or $R^8\text{-}POBr_2$), a dihalophosphine sulphide ($R^8\text{-}PSCl_2$ or $R^8\text{-}PSBr_2$), sulphuryl chloride (SO_2Cl_2), thionyl chloride ($SOCl_2$) or ethylaluminium dichloride ($C_2H_5AlCl_2$) and recovering the ligand.

20. Process for the preparation of polymers, wherein a mixture of carbon monoxide and one or more olefinically unsaturated compounds is polymerised in the presence of a

catalyst composition as claimed in any one of claims 1-13.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 00/06402

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08G67/02 B01J31/18 C07F9/50 C07D319/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08G B01J C07F C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 296 687 A (SHELL INT RESEARCH) 28 December 1988 (1988-12-28) cited in the application column 2, line 37 - line 44; claims 1,3,6 column 3, paragraph 2 -column 4, line 13 column 4, paragraph 3; example 1	1-3, 5-11, 14-17,20
X	EP 0 300 583 A (SHELL INT RESEARCH) 25 January 1989 (1989-01-25) claims 1,3,4,6 column 5, line 11 - line 19	1-3,5-7, 9-11, 14-17,20

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
19 September 2000	01.12.00

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Lauteschlaeger, S

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 743 336 A (SHELL INT RESEARCH) 20 November 1996 (1996-11-20) claims 1,11,12 page 4, line 40 - line 49 page 4, line 14 - line 20 ---	1-3, 5-11, 14-17,20
A	US 4 851 461 A (NELSON RICHARD V ET AL) 25 July 1989 (1989-07-25) cited in the application column 4, line 55 - line 65 -----	1-20

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International application No.
PCT/EP 00/06402

INTERNATIONAL SEARCH REPORT

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1 - 20: Partly

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1 - 20: Partly

Claims 1 and 16 (and subclaims thereof) disclose various catalysts and their intermediates (ligands); claim 18 discloses a process for obtaining the aforementioned intermediates.
The catalysts as claimed contain ligands wherein Y represents a variety of functional groups.
1. Catalysts containing ligands with Y being a functional group the central atom of which is a Main group IV element (C or Si), are known (cf. documents D1 - D3 (citations in the Search Report)).
2. The remaining subject-matter relates to 3 distinct and unrelated embodiments (catalysts containing ligands with Y = functional groups the central atom of which is a Main group III (Al) or V (P) or VI (S) element) which obviously do not exhibit mutual structural features.
A unifying novel and inventive concept common to the different compounds cannot be discerned.

3. The parts of claims 1 - 20 covered by the present Search are those defining catalysts (or ligands as such) (or their process of production) containing ligands wherein Y represent a functional group the central atom of which is C or Si.

4. It is noted that claims or part of claims for inventions not covered by the Search, can normally not be taken into account in the IPER (Rule 66.1(e) PCT). No preliminary examination will thus be made for the afore-mentioned embodiments not covered by the present search if the Applicant refuses to pay additional fees.

2. Claims: 1-20: Partly

see subject 1, point 2.

3. Claims: 1-20: Partly

See subject 1: Point 2.

4. Claims: 1-20: Partly

See subject 1: Point 2.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 00/06402

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